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Dynamic separation of electron excitation and lattice heating during the photoinduced melting of the periodic lattice distortion in 2H-$TaSe_2$

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The photoinduced structural dynamics in 2H-$TaSe_2$ in the charge-density wave (CDW) state is investigated using MeV ultrafast electron diffraction. By simultaneously tracking both the melting of the periodic lattice distortion (PLD) associated with the CDW and the lattice heating, following an impulsive photoexcitation, the separate contributions of electronic excitation and lattice thermalization to the melting process are disentangled in the time domain. Two distinct time-constants, reflecting the corresponding individual dynamics of the subsystems, are observed. Our experimental results demonstrate that the PLD in 2H-$TaSe_2$ is first suppressed promptly by the electronic excitation and scattering, and then subsequently by lattice thermalization through electron-phonon interaction, on a much longer time scale. This latter leads to the final, full melting of the PLD. [http://dx.doi.org/10.1063/1.4818460]

As prototypical low-dimensional materials, transition metal dichalcogenides are model materials for charge-density wave (CDW) transitions and strong electron-phonon interactions and are therefore a much studied test bed for exploring the interactions of electrons with lattice degrees of freedom. Developing a detailed understanding of these remains an important issue of current condensed matter research, especially in the strongly correlated electron materials, where the effects of electron-phonon interactions are hotly debated. Over the years, intense theoretical and experimental efforts have been devoted to the understanding the origin of the CDW and the relationship between the electronic modulation and the periodic lattice distortion (PLD) in these quasi-two-dimensional anisotropic compounds.[1–3] Despite this effort, however, the microscopic mechanism underlying the CDW formation remains unclear, and there are even some disagreements among the various experimental techniques over such basic quantities as the measured CDW gap.[4] This lack of clarity may be attributed to the complicated interplay among the various orders in these coupled electron-lattice systems and to the inability of conventional, that is time-averaged, techniques to disentangle these interactions under equilibrium conditions.

Recently, ultrafast time-resolved probes have provided a different approach for studying the CDW dynamics in these materials.[5–11] Taking advantage of the different characteristic time scales of the various subsystem dynamics, ultrafast measurements with femto-second time resolution have the unique ability to differentiate the respective contributions of the different subsystems to the CDW dynamics by working in the time domain. In addition, ultrafast probes can also reveal, and trace, any possible transient hidden states involved, providing more insights into the mechanisms driving the formation of the CDW.[5,12] Early time-resolved studies were mainly based on photoemission and ultrafast optical methods which probe the electronic structure and response, respectively. The related structural changes then had to be extracted through sophisticated theoretical modeling.[5–7,9–11] More recently, ultrafast diffraction methods, which can provide a direct real-time view of the structural changes,[13–16] have been used to probe the dynamics of the optical suppression of the PLD.[8,17,18] In this letter, we report MeV ultrafast electron diffraction (UED) measurements of the melting of the PLD in 2H-$TaSe_2$, driving the phase transition from the commensurate CDW state to the normal metallic state by photoexcitation. By simultaneously observing the response of both the PLD and of the average lattice—by studying the super-lattice (SL) reflections and the Bragg and diffuse scattering, respectively—the contributions of the electronic excitation and of lattice thermalization to the melting of the PLD are disentangled in the time domain. The results indicate that the PLD undergoes an initial fast decay following electronic excitation but partially survives to 1 ps after which lattice thermalization fully melts the PLD.

2H-$TaSe_2$, a transition metal dichalcogenide, is one of the most-studied quasi-two-dimensional CDW systems.[2,19–22] It possesses a simple crystal structure, consisting of planes of hexagonally arranged tantalum (Ta) atoms, sandwiched by two selenium (Se) layers coordinating the central Ta atom in a trigonal prismatic arrangement. At low temperatures, a CDW forms, modulating the conduction electron density, together with a concomitant lattice distortion, known as the PLD, in which the Ta atoms are grouped into seven-atom clusters.[4] 2H-$TaSe_2$ has a complicated phase diagram that exhibits a

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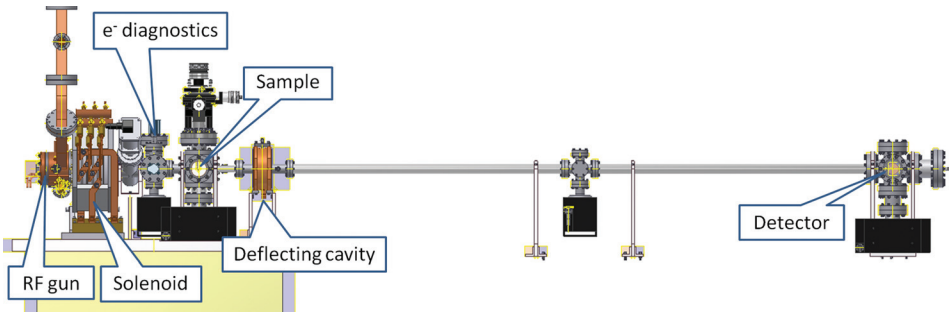

FIG. 1. Schematic of the MeV-UED set-up. The entire system is ~4.5 m long.

series of successive phase transitions with the temperature. Upon cooling, the transition from a metallic state to an incommensurate CDW phase occurs at $T_{m-i} = 122$ K, followed by a first-order phase transition from the incommensurate CDW phase to a 3×3 commensurate CDW phase at $T_{i-c} = 88$ K. On warming, there is significant thermal hysteresis and the system passes through another series of phases.

Here, we utilize UED with MeV electrons to carry out this work. The basic principle of MeV-UED is similar to that of the previous UED experiments based on DC electron guns running at 30–100 keV, which have been widely used in ultrafast science in the last decade.[13–16] The use of relativistic electrons, however, offers several advantages over lower energy electrons: Specifically, an over two orders of magnitude increase in the number of electrons per bunch, a shorter electron pulse length, a larger electron beam penetration depth, and a much reduced pump-probe velocity mismatch.[23–25] Fig. 1 shows a schematic of the MeV-UED set up at Brookhaven National Lab. The unique feature of MeV-UED is the use of a photocathode RF gun to generate the femtosecond electron pulses with MeV kinetic energy. MeV-UED has been under rapid development since it was first proposed[26] and has recently demonstrated sufficient signal-to-noise ratio (SRN) to observe SL peaks in diffraction patterns, together with femtosecond time resolution.[27]

The 2H-$TaSe_2$ sample is fabricated as a free standing film of ~150 nm, as determined through electron energy loss measurements and modeling approaches using a 300 keV TEM. The samples were then mounted on the temperature stage of a flow cryostat inside an ultra high vacuum (UHV) chamber. Diffraction patterns are obtained in transmission mode with the electron beams normally incident on the $TaSe_2$ film. All data were taken with the sample at ~80 K, i.e., below the commensurate transition temperature, $T_{c-i} = 92$ K. The dynamics was initiated by a 150-fs laser pump at 795-nm wavelength. A series of diffraction patterns were then recorded for different time delays between the optical pump and the electron probe, to track the subsequent photoinduced structural evolution. The penetration depth at 795-nm is greater than 100 nm (Ref. 9) and the pump laser beam on the sample is much larger than the electron spot size. Thus, the photoexcitation is quite uniform over the entire probed area.

A typical diffraction pattern from $TaSe_2$ in the CDW state is shown in Fig. 2(a). The image intensity has been rescaled to highlight the weak SL peaks. Each Bragg peak, i.e., the large bright spots arising from the primary lattice, is surrounded by six SL peaks originating from the commensurate PLD order, with a wavevector $\mathbf{q} = 1/3\mathbf{a}^*$, and symmetry related positions. Fig. 2(b) displays the diffraction intensity distribution along the yellow line in Fig. 2(a), and clearly shows the SL peaks between the Bragg peaks, reflecting the existence of the PLD. It is worth noting that despite the fact that the amplitude of the PLD in 2H-$TaSe_2$ is quite small,[4] and consequently, the SL is much weaker than that of 1T-TaS_2,[28] the SL peaks are still clearly observable and are recorded with a good SNR, attesting to the high beam quality and sensitivity of the MeV-UED setup.

Our focus here is to reveal the dynamics of the PLD melting as initiated by an impulsive photoexcitation. The pump fluence is 1.4 mJ/cm^2 per pulse and the sample base temperature was ~80 K. The estimated sample temperature jump after each pump pulse is about 45 K. Thus, the sample was heated up to ~125 K and driven across the phase transition into the metallic phase a few ps after the arrival of the optical pump pulse. The system recovered back to the CDW state before the next laser pulse arrived, as confirmed by observing the vanishing and re-appearance of the SL peaks with each pulse.

To trace the melting dynamics of the PLD, the temporal evolution of the SL intensity was monitored in real time. The data in the first 5 ps are shown in Fig. 3(a). The SL intensity is taken to be the difference between the intensity summed over the SL areas around a particular Bragg peak minus the background diffuse scattering. This latter is measured at the same magnitude of momentum transfer relative to the host Bragg peak as the SL peak. This procedure ensures that we measure the dynamics of the SL peak, which is distinct from the dynamics of the diffuse scattering, as discussed below.

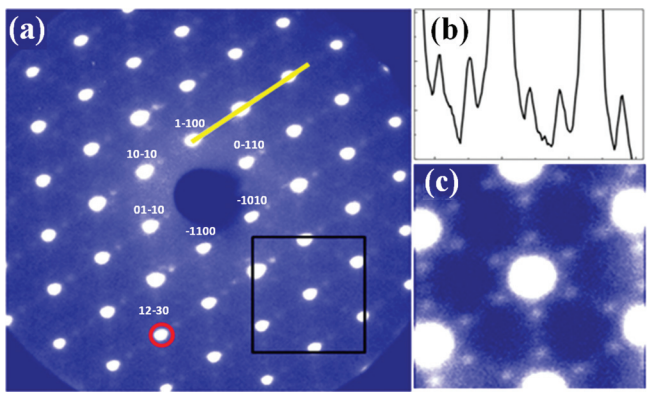

FIG. 2. MeV UED diffraction data from 2H-$TaSe_2$ in the CDW/PLD state. (a) Diffraction pattern obtained from a 200-shot accumulation at T = 80 K. The intensity has been rescaled to emphasize the SL peaks. (b) The intensity distribution along the yellow line in (a). (c) Diffraction pattern obtained after averaging 10 identical boxes in (a).

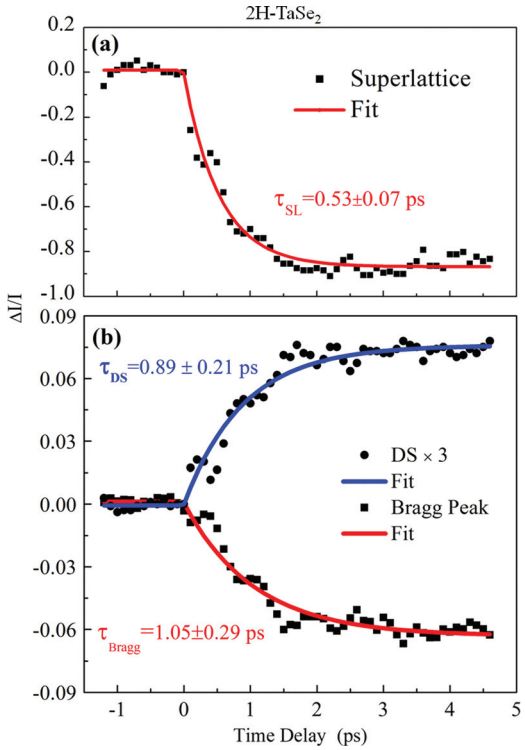

FIG. 3. (a) Temporal evolution of the SL peak. (b) Temporal evolution of the Bragg peak and diffuse scattering intensity. For clarity, the change of diffuse scattering intensity is multiplied by 3. The pump was a 795 nm optical pulse, at a fluence of 1.4 mJ/cm^2. The solid lines with given time constants are fits to the experimental data using an exponential function.

Following the laser excitation, the SL intensity shows a prompt drop and is reduced nearly to zero within the first 2 ps. Further experiments show that there is no obvious recovery in the following 50 ps. Fitting of the time dependence of the intensity to a single exponential for the entire 5 ps range yields a time constant of 0.53 ± 0.07 ps.

In addition to the SL peak, the intensity of both the Bragg peaks and of the diffuse scattering may also be extracted from the diffraction patterns. To improve the SNR of these data, the Bragg peak intensities were averaged over 12 peaks of the same symmetry. The family of reflections of type ⟨12–30⟩ was chosen for its relatively large momentum transfer. One such peak is marked by a red circle in Fig. 2(a). The diffuse scattering intensities were calculated by summing the intensity of the areas between the 6 surrounding SL spots for a given Bragg peak (Fig. 2(c)). Fig. 3(b) shows the temporal evolution of the relative change of these Bragg peaks and of the associated diffuse scattering, following photoexcitation. The data show that the Bragg peak intensity drops while the diffuse scattering intensity simultaneously increases, with time constants of 0.89 ± 0.21 ps and 1.05 ± 0.29 ps, respectively. That is, to within errors, they have the same time response. The temporal evolution of these peaks demonstrates that the average lattice order is indeed disturbed following femto-second optical excitation. Further, the evolution occurs on a much slower time scale than that of the PLD—about a factor of two longer than that of the average time constant extracted above.

In the previous UED studies of CDW photoinduced dynamics, in 1T-TaS_2[8] and in $4H_b$-$TaSe_2$,[17] it was found that the Bragg peak intensity increased after the initial electron-heating-induced partial melting of the CDW. No such enhancement is observed in the current study. This difference is due to the different amplitudes of the PLDs induced by the respective CDWs in the different systems. Specifically, the lattice distortion is 7.5% in 1T-TaS_2 and only 1.5% in 2H-$TaSe_2$.[4] As a result, the relative SL peak is roughly 25 times weaker in the 2H-$TaSe_2$ system. As pointed out previously,[8] the rise in the Bragg intensity seen in other systems comes from the restoration of the average lattice, following optical suppression of the PLD, and before lattice thermalization becomes significant. That is, the increase is effectively a transfer of scattered intensity from the SL peak to the Bragg peak, before lattice vibrations significantly reduce the Bragg peak due to Debye-Waller-like effects. Since the initial SL peak is so weak in the present case, it makes only a very small contribution to the Bragg peak and one cannot observe that contribution. Hence we only see the Bragg peak decrease in the present case. We note that similar behavior is seen in $CeTe_3$,[17] presumably for the same reason. As the lattice starts to thermalize with the hot electrons, one sees the Bragg peak intensity drop, as a result of the thermal lattice vibrations. This transfers intensity from the Bragg peaks to the diffuse scattering in a one-to-one correspondence, which is why these two have identical time constants.

Earlier work has discussed optical suppression of the PLD in terms of a picture in which the optical pulse initially excites the electron subsystem to very high temperatures and that this causes a very fast suppression of the amplitude of the PLD. Subsequently, as the electrons begin to thermalize with the lattice via the electron-phonon coupling, the resulting atomic vibrations reduce the amplitude of the PLD further and cause a reduced Bragg peak intensity and increased diffuse scattering through a Debye-Waller-like effect,[8,17,18] In this present work, we are able to discern these steps explicitly because of the improved time resolution of the present set-up and because of the weakness of the lattice distortion, which allows a clean separation of the PLD and average lattice dynamics, such that, as discussed above, the Bragg and diffuse intensity only reflects the latter.

With this understanding in hand, there are a number of interesting features to the present observations. First, the different time constants observed in the photo-induced dynamics of the PLD melting and the primary lattice perturbation clearly indicate that the photo-induced dynamics in 2H-$TaSe_2$ involves multiple steps occurring at different time scales. Specifically, the initial high-temperature electron impulsion gives rise to the prompt behavior in the beginning. This corresponds to heating of the electron subsystem up to several thousand Kelvin within a few tens of femto-seconds and subsequent electron thermalization via electron-electron scattering. During this time the lattice remains nearly unperturbed.[29] This prompt temperature rise creates a strong non-equilibrium between the electron and lattice subsystems,[6,12] which changes the potential surface[30] and also partially destroys the charge order[7] established under the initial equilibrium conditions. While this regime has been inferred in earlier studies,[8,18] it is particularly clear here because of the distinct timescale of melting of PLD from that of lattice heating as measured by MeV-UED.

Subsequent to this electron heating, the energy is transferred from the hot electrons to the lattice through the electron-phonon coupling. This process occurs on much longer time scales and continues until the electrons and lattice reach a thermal equilibrium. This is evidenced in the behavior of the Bragg peak and diffuse scattering, which show a time constant of ~1 ps for this process, which is related to the creation of incoherent phonons. During this process, the PLD is suppressed with a 0.53 ps time constant, which is a factor of two faster. This is in contrast with the behavior observed in the related system 4H-$TaSe_2$ where the same time constant was observed for the PLD and Bragg peak behaviors. However, we note that there is no reason *a priori* that these should be the same. In fact, there are a number of reasons that these could be different. First, the Bragg peak and diffuse scattering behavior reflects the incoherent sum of all phonon modes, whereas the PLD is most sensitive to the amplitude mode of the CDW distortion (that is the mode that freezes to create the PLD in the first place). This can certainly have different temporal behavior. Second, the PLD transition temperature is relatively low in this material ($T_{m-i} = 122$ K) and the decay of the order parameter with (lattice) temperature will have the effect of appearing to speed up the melting process relative to the creation of an incoherent phonon bath.

Previous time-resolved photoemission studies have shown that the photoinduced CDW melting finishes on the 100 fs time scale,[5–7,11] i.e., faster than the dynamics of the PLD observed in this and earlier experiments.[8,17,18] As discussed above, the full melting of the PLD requires that the lattice thermalize to a temperature above the CDW transition temperature and occurs on the timescale of the electron-phonon interaction. Therefore, unlike the closing of the CDW gap, which is a purely electronic phenomenon, the PLD is not completely destroyed by merely raising the electronic temperature to a few thousand degrees above the transition temperature.[8,17,18] The fact that some remnant of the PLD survives beyond 1 ps may play an important role in the reconstruction of the CDW on sub-ps time scale after the CDW is destroyed by an impulsive photoexcitation observed in the previous study,[10,12] the inertia of the lattice preserves some of the PLD order, which helps, to some extent, the faster recovery of CDW during the subsequent sub-ps electron cooling.[7,17]

Finally, we note the presence of apparent oscillations in the all three temporal curves. While it was not possible to definitively resolve these oscillations in the data, there are strong correlations in the three data sets with an approximate frequency of 2.5 THz. This is consistent with the amplitude mode frequency as observed in time-resolved angle-resolved photoemission spectroscopy (ARPES) studies of the CDW and Mott gaps in 1T-TaS_2.[6,10,11] Further experiments with improved SNR may reveal more details about the relation between electron modulation and PLD in this transient phase.

In conclusion, the femto-second MeV-UED experiment on a complex material was performed to understand the ultrafast dynamics during photoinduced melting of the PLD in 2H-$TaSe_2$. The temporal evolution of both the PLD and the primary lattice order are observed and differentiated in the time domain on a sub-ps timescale. This temporal separation allows one to observe the melting dynamics under highly non-equilibrium conditions and makes it possible to distinguish the response of the PLD to electronic excitation and lattice thermalization, and their relative roles in the melting of the PLD. The experimental results suggest that the PLD in 2H-$TaSe_2$ can at least partially survive the presence of a high-temperature electronic subsystem and that its complete melting is dominated by the lattice heating. The study of the long-lived PLD dynamics may shed more insight into the mechanism of CDW formation.

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